Compositional Dependence of Electromechanical Behavior of Ba,Zr-Codoped Sodium Bismuth Titanate

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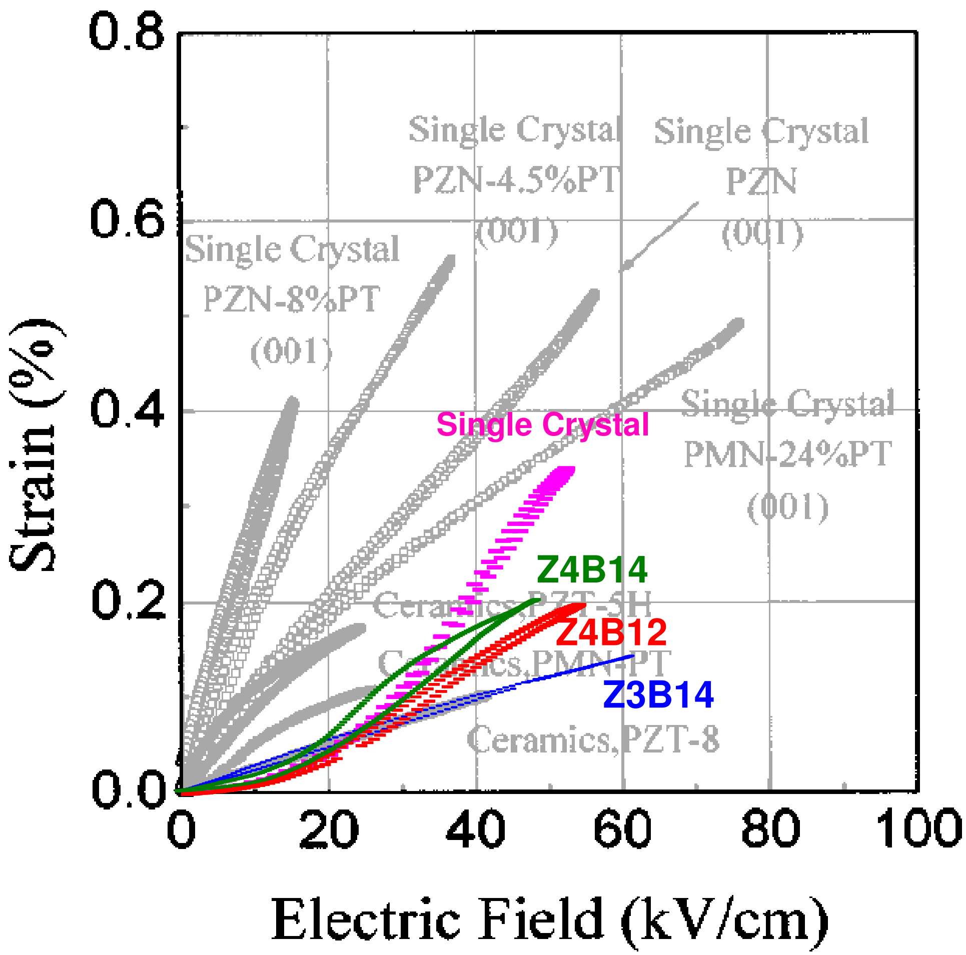
Outline

- Introduction: doped $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) as the best high-strain lead-free competitor of lead-relaxors
- Studied compositions and experimental setup
- Diverse electromechanical behavior
- Free energy expansion and phase diagram
- Nanostructure imaged by TEM

Doped NBT as a lead-free alternative

$Na_{1/2}Bi_{1/2}TiO_3$ polycrystals† vs. lead perovskites*

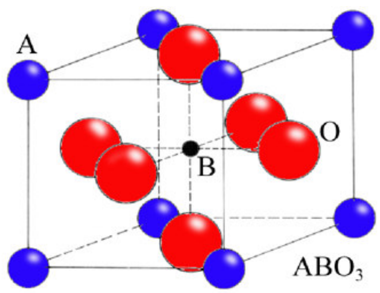


– New Lead-Free actuator materials
– High strain at high fields
– Polycrystals with actuation comparable to PZT-8, PMNT
– Single crystals 2x higher ultimate strain

† Y.-M. Chiang group (MIT).

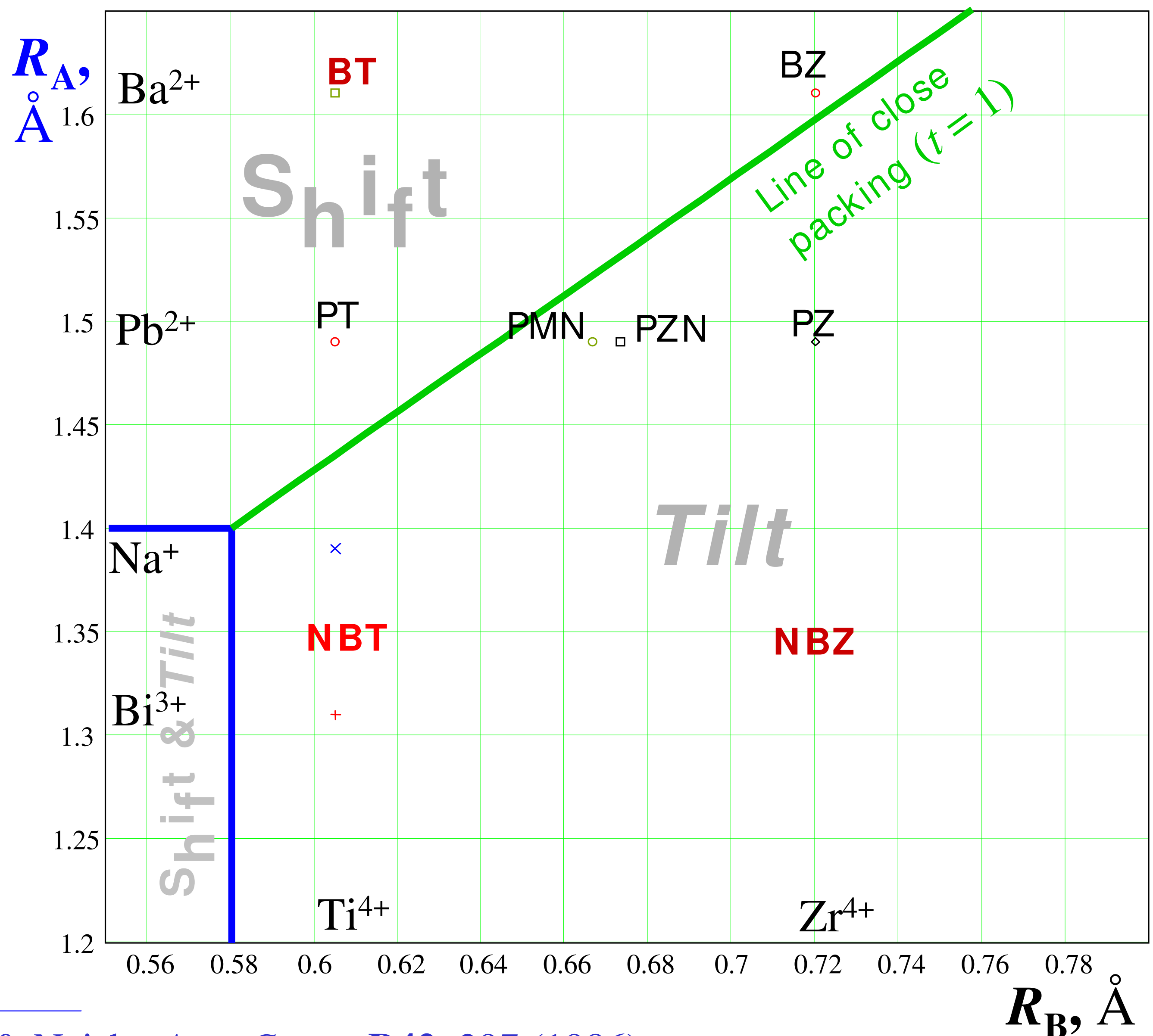
* Park & Shrout, 1997.

Map of Distortions in Perovskites ABO_3*



Goldschmidt tolerance factor:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

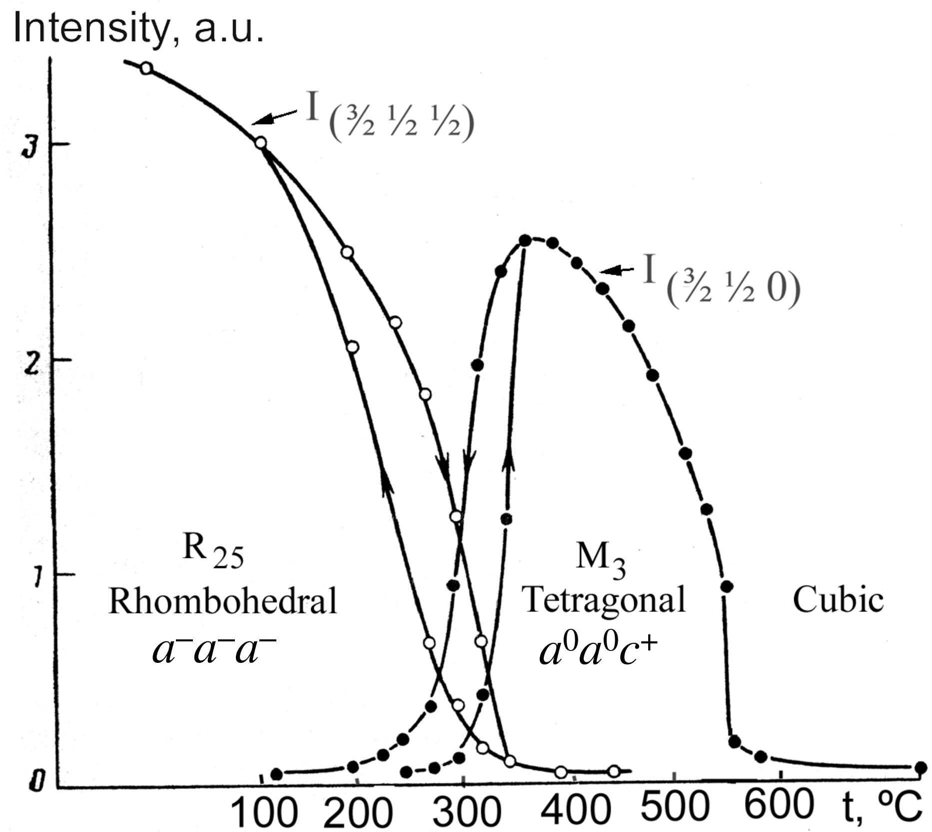


* Kassan-Ogly & Naish, *Acta Cryst.* **B42** 297 (1986)

Phases of NBT

*R*3*c* ↔ *P*4*bm* ↔ *Pm*$\bar{3}$*m*

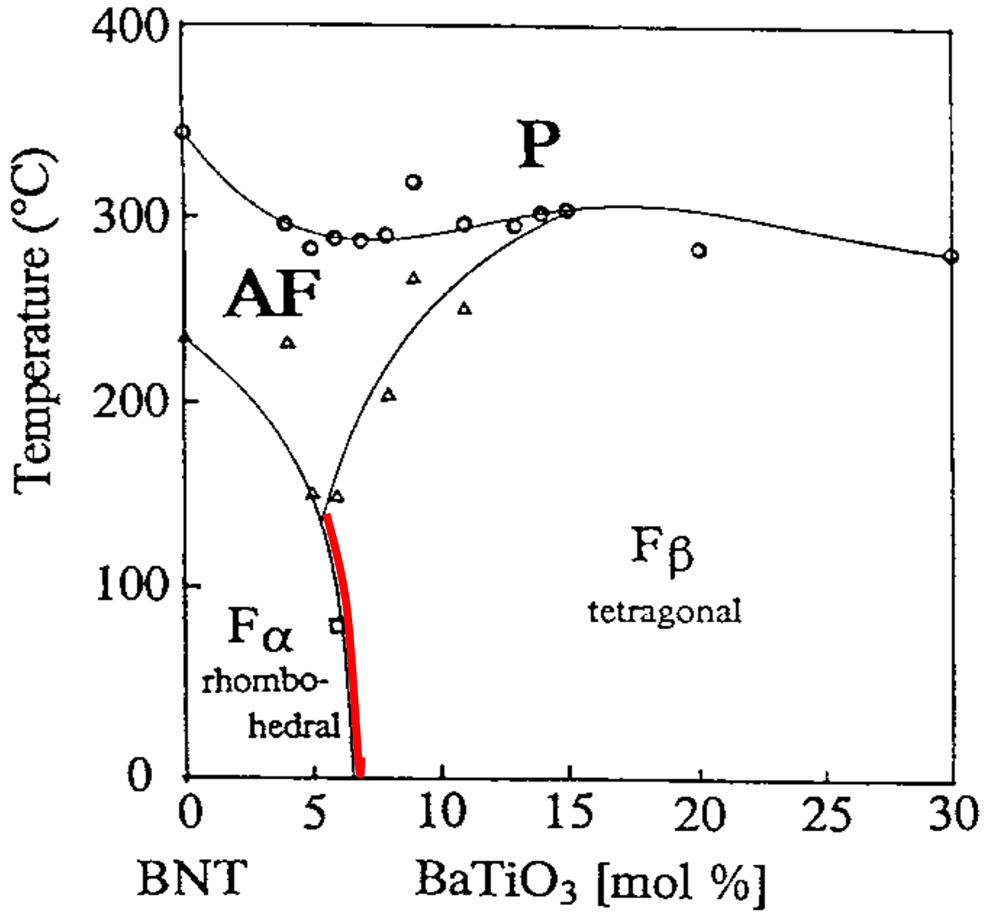
Jones & Thomas, *Acta Cryst.* **B58**, 168-178 (2002).



Intensities of octahedral tilt superlattice reflections vs. temperature – neutron diffraction data for single crystal NBT.

Vakhrushev *et al*. *Ferroelectrics* **63** [1-4] 153-60 (1985).

NBT-BT Solid Solutions



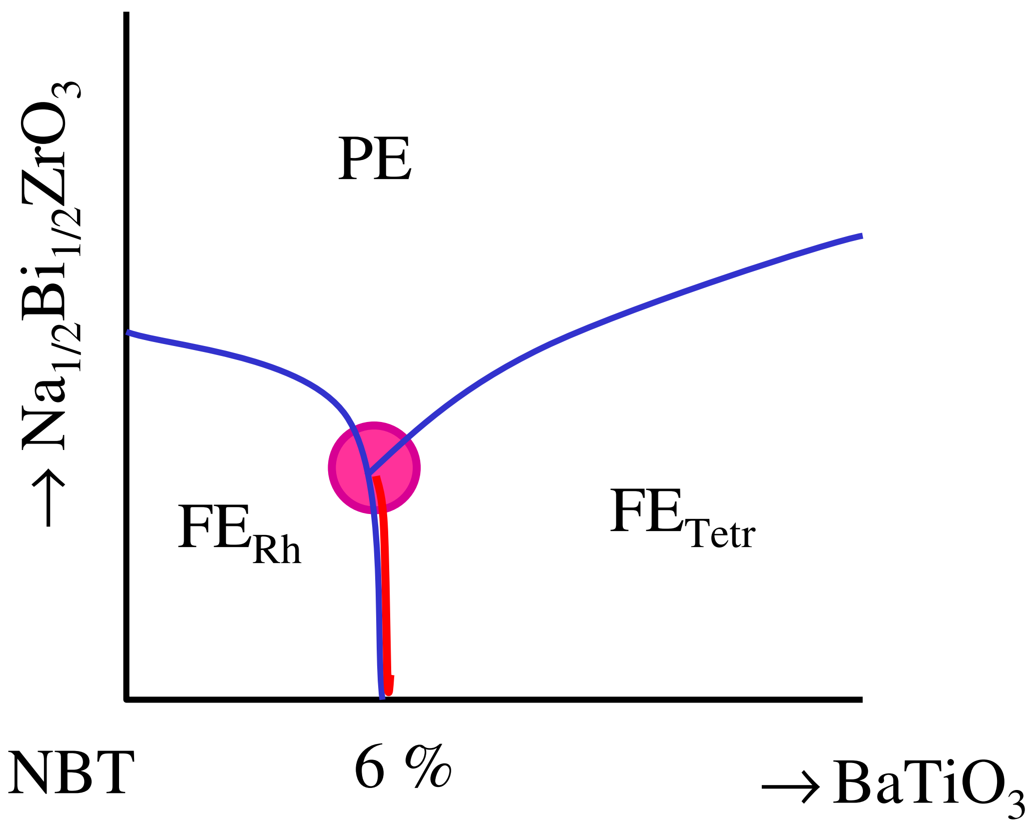
BNT–$Na_{1/2}Bi_{1/2}TiO_3$, F–ferroelectric phase, AF–antiferroelectric phase, P–paraelectric phase

Takenaka *et al.*, *Jap. J. Appl. Phys.*, **30** [9B], 2236 (1991)

Compositions close to morphotropic phase boundary (MPB) at 6% BT exhibit enhanced piezoelectric performance

$(Bi_{1/2}Na_{1/2})_{1-x}Ba_xZr_yTi_{1-y}O_3$ (BNBZT)

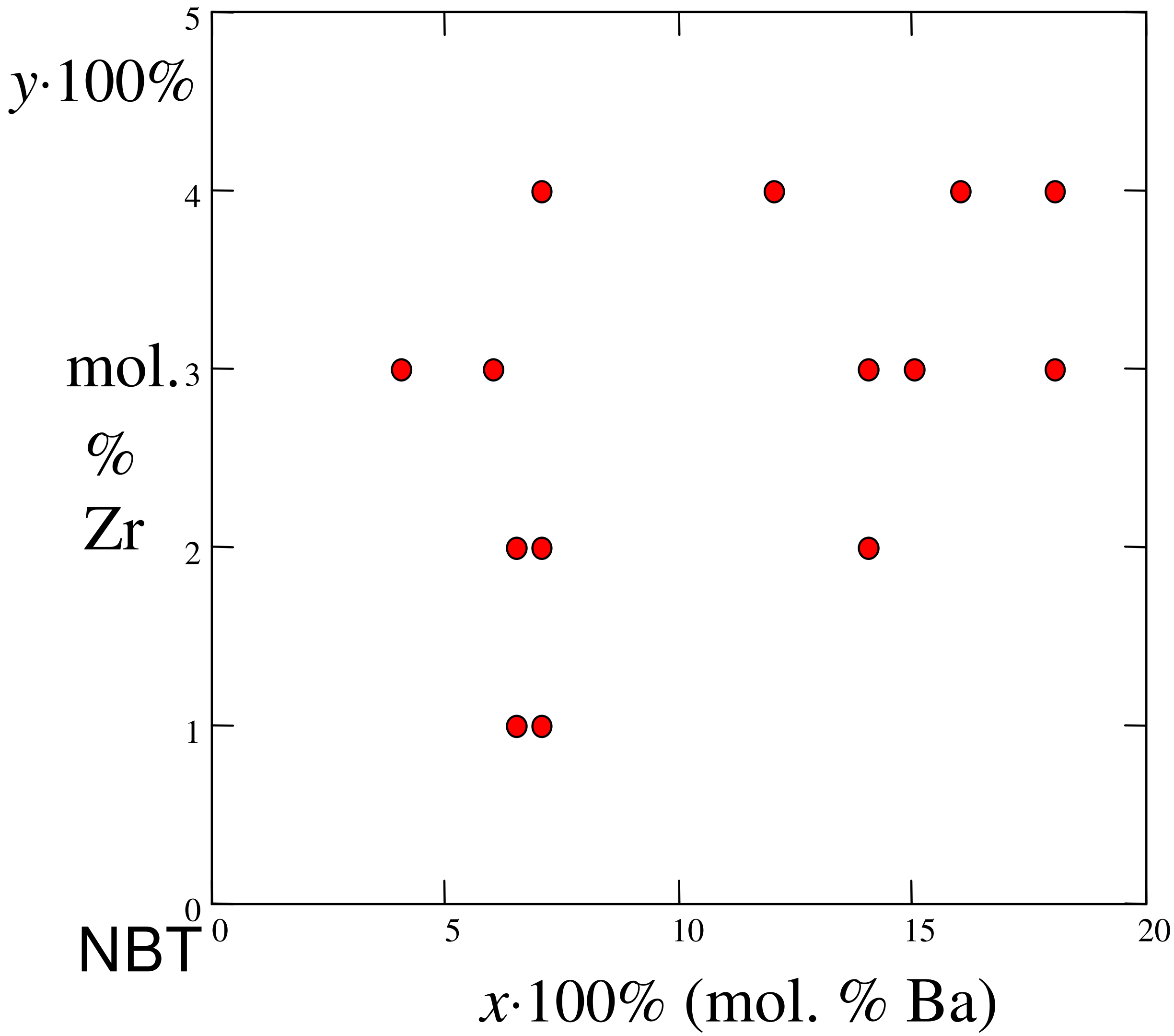
Hypothetic Phase Diagram



- Zr on B-site suppresses ferroelectricity*, so at some concentration the phase should become paraelectric (PE)
- Termination of the Rh-Tetr boundary is a **tricritical point** at which electromechanical response should reach its maximum

* Rossetti, *J. Solid State Chem.* **144** (1) 188-194 (1999)

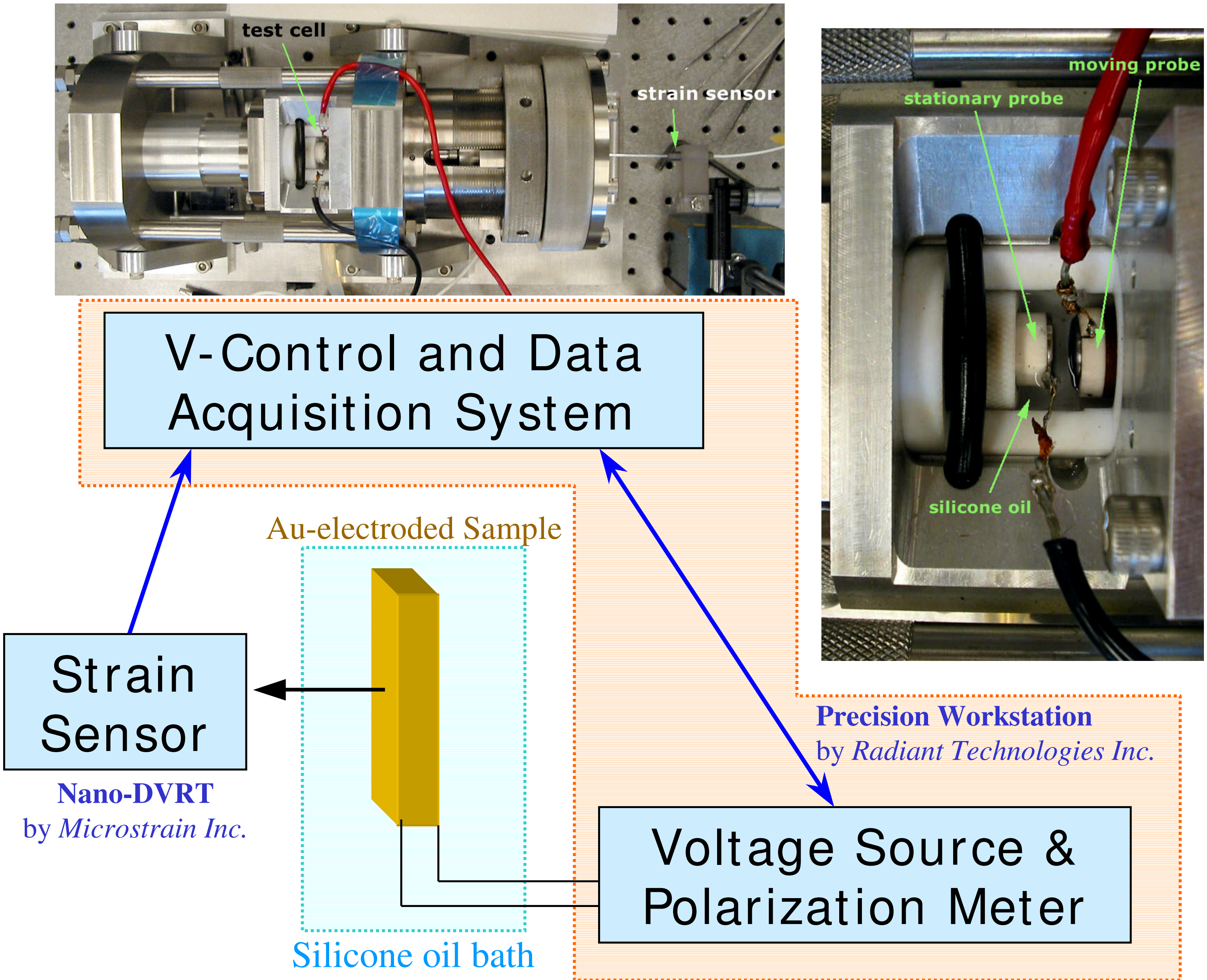
Electromechanically Tested Polycrystalline $(Bi_{1/2}Na_{1/2})_{1-x}Ba_xZr_yTi_{1-y}O_3$ (BNBZT) Samples



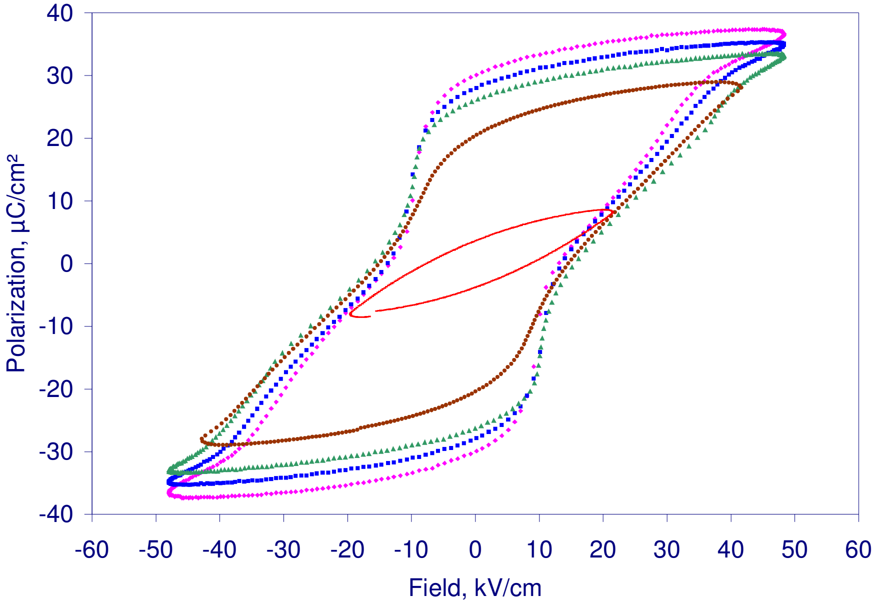
- Samples by solid state synthesis method, sintered into ∅10 mm disks with >95% density:

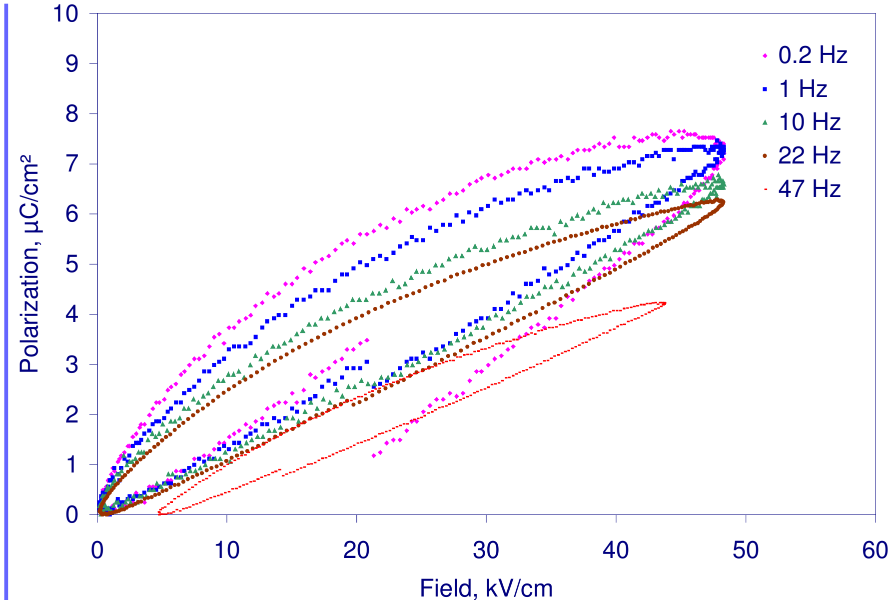
- Composition was confirmed by EPMA
- >98% perovskite phase purity was confirmed by XRD

Electromechanical Testing Setup

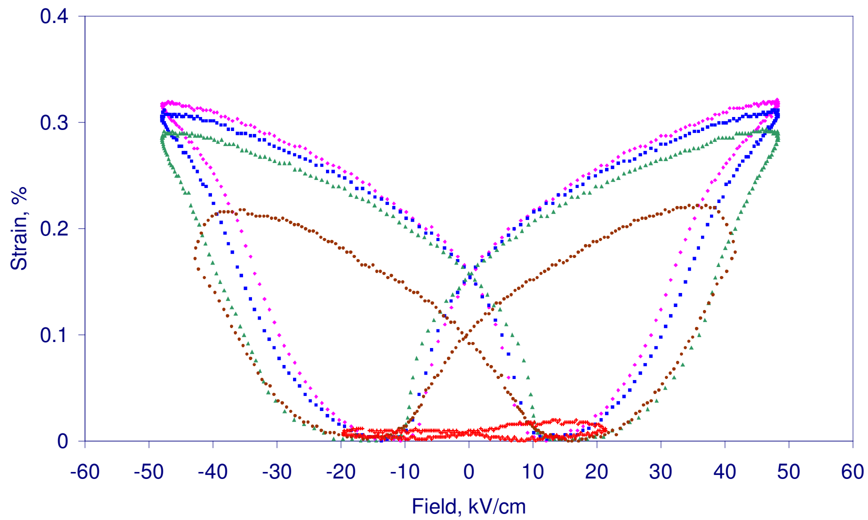


Electromechanical Behavior of BNBZT with 1% Zr and 7% Ba (z1b7)

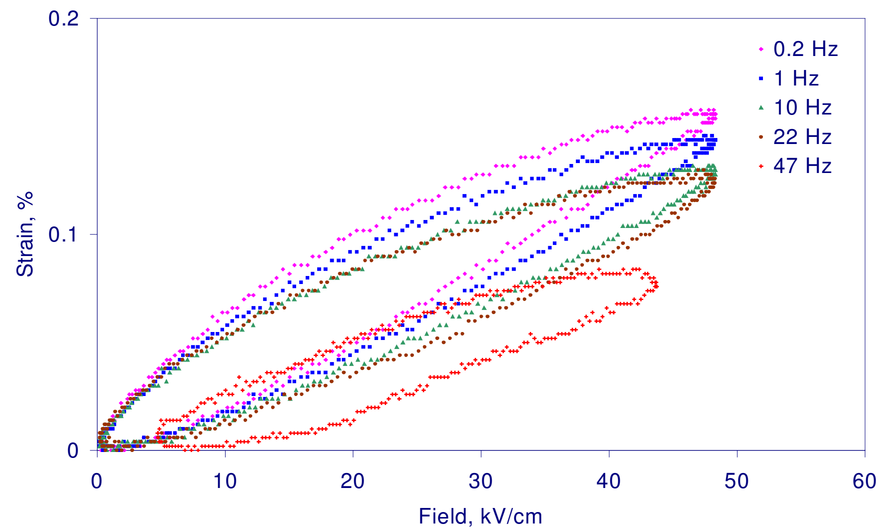




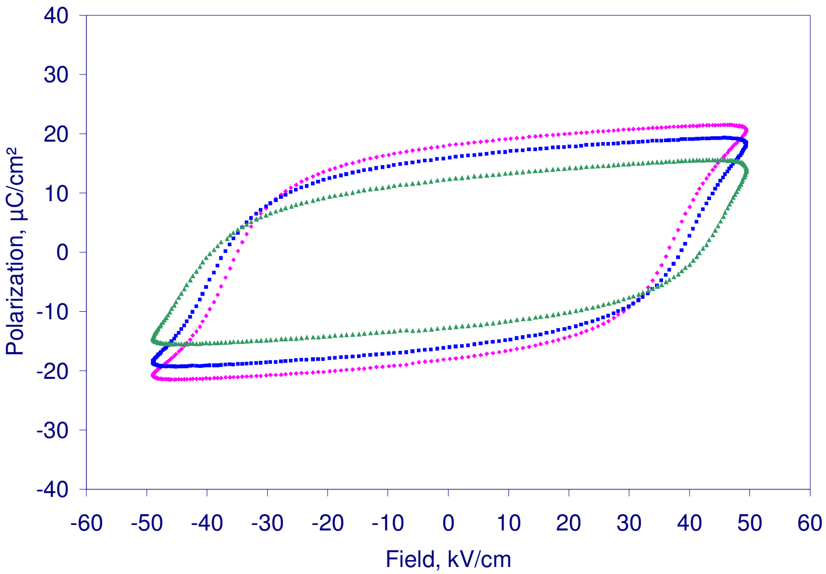
Bipolar actuation

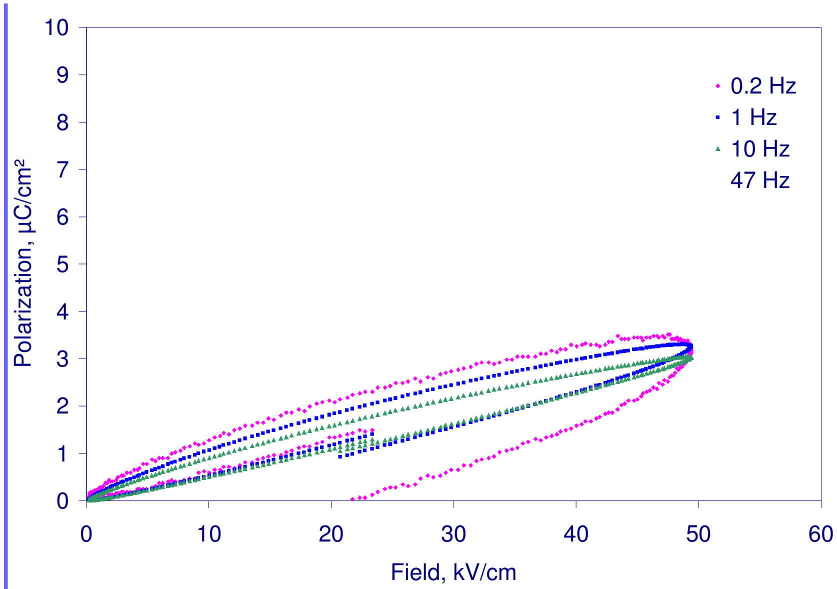


Unipolar actuation



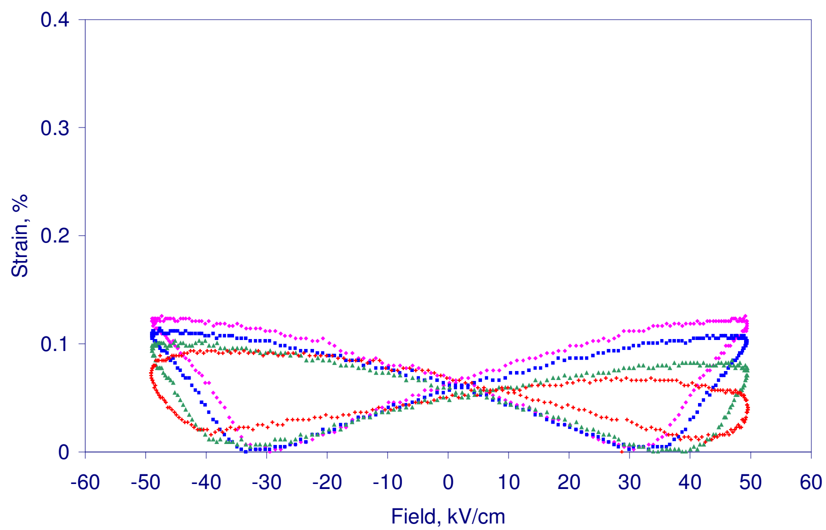
Electromechanical Behavior of BNBZT with 3% Zr and 4% Ba (z3b4)

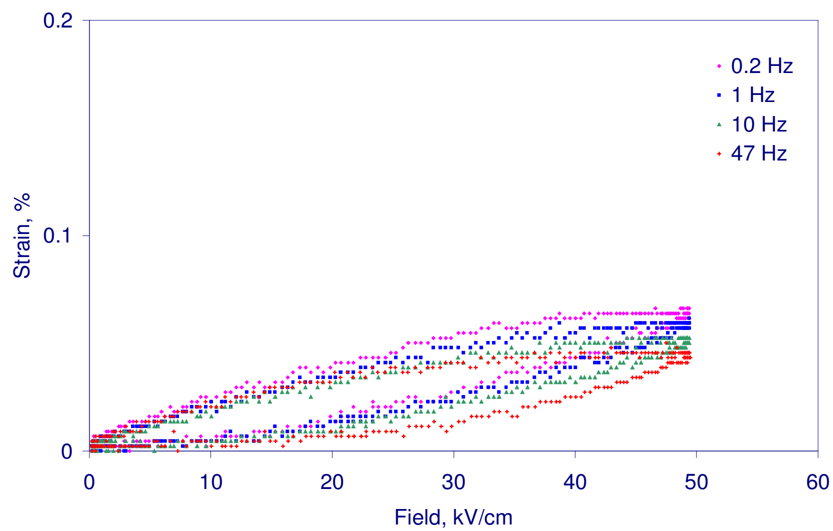




Bipolar actuation

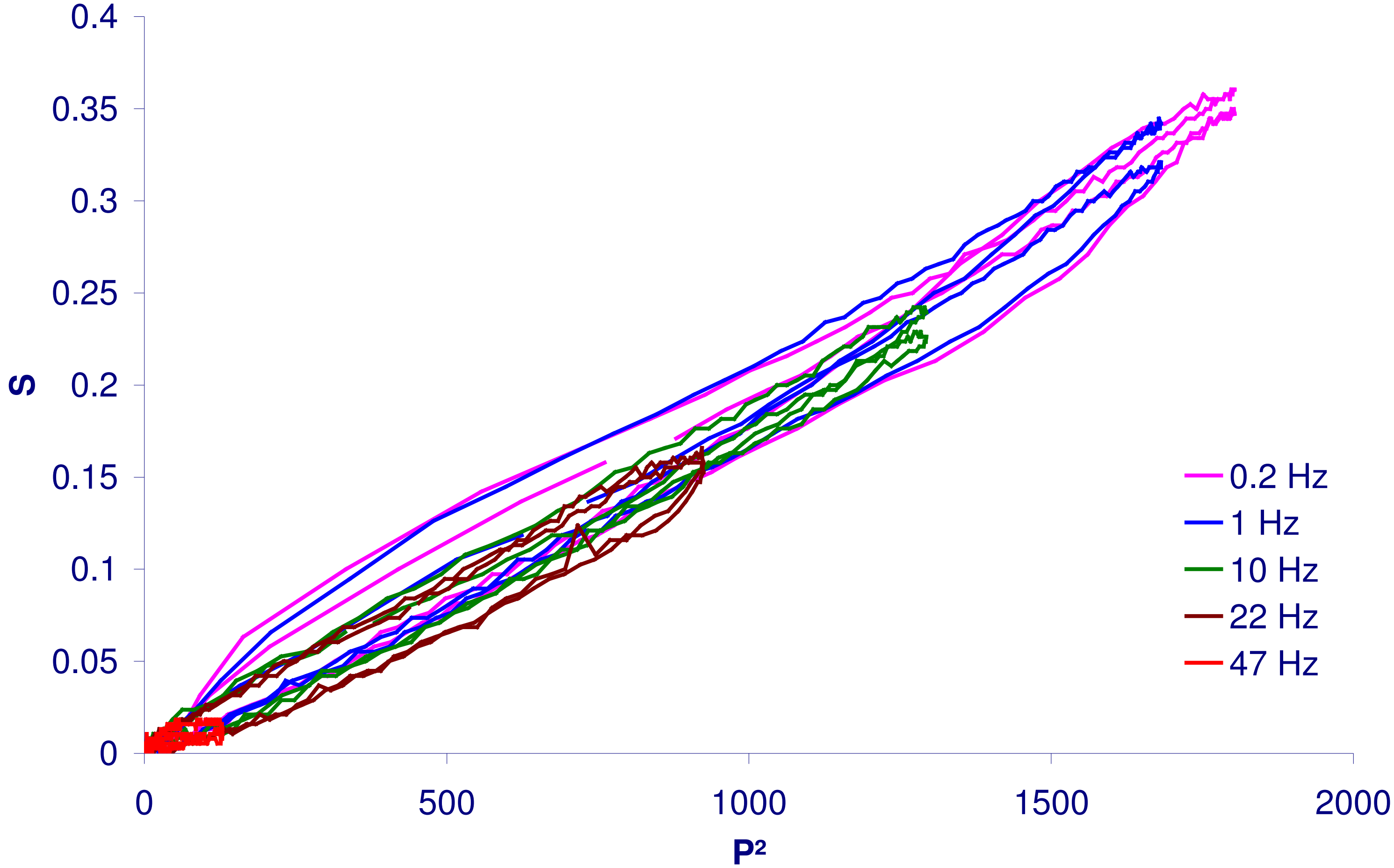
Unipolar actuation





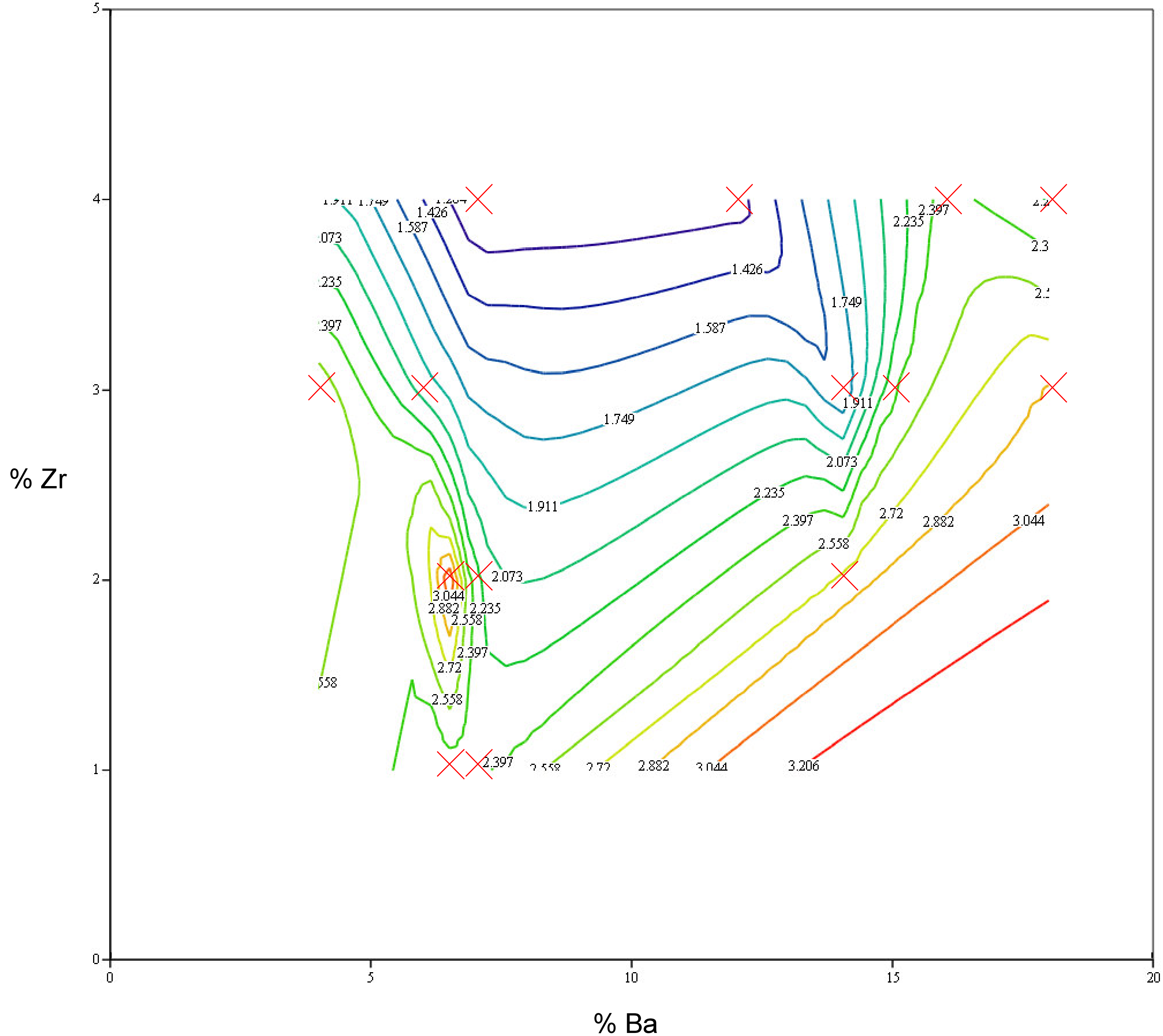
Frequency Independent Electrostrictive Relation

$$S = Q\,P^2$$

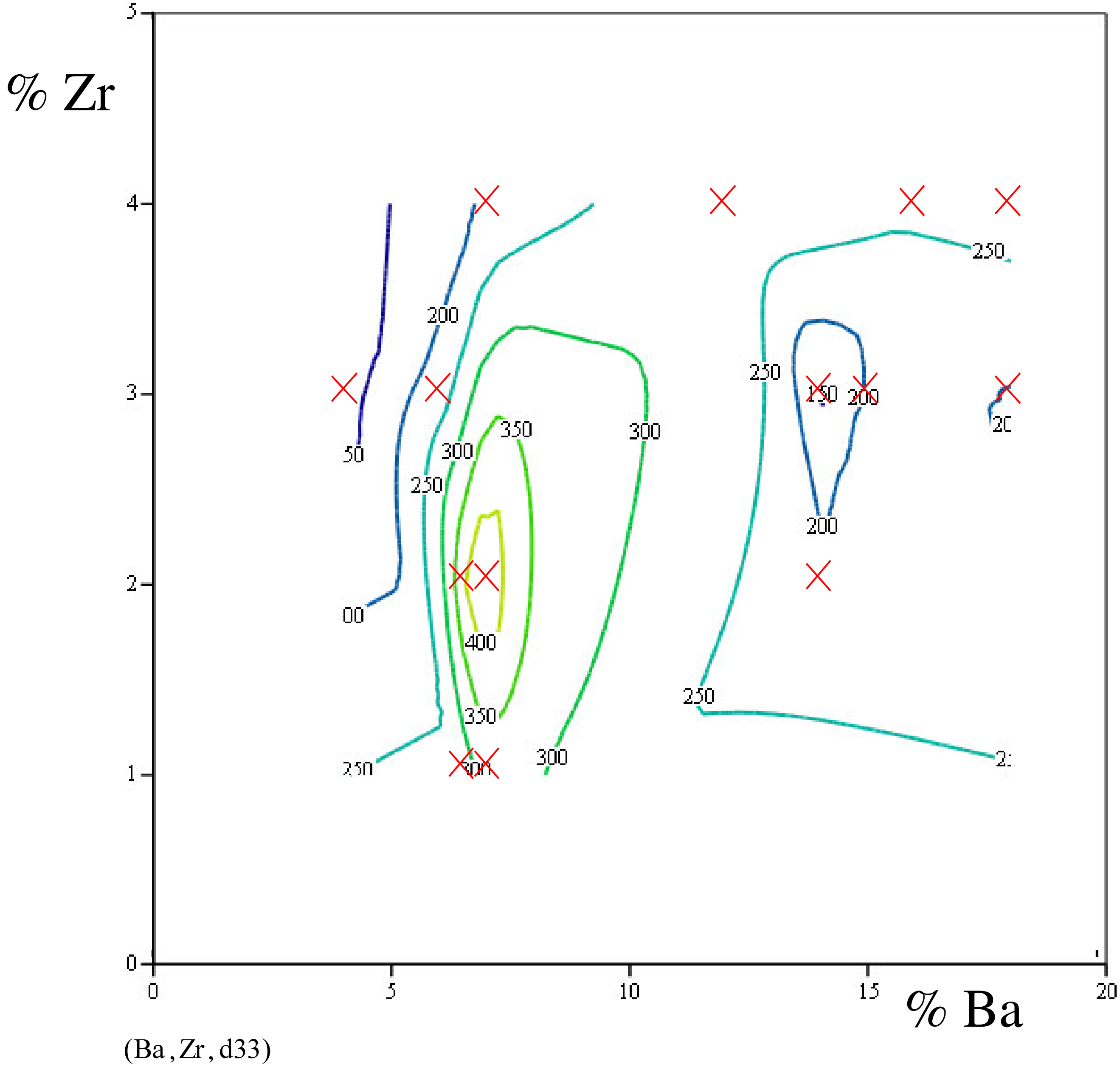


Typical for **all samples** bipolar strain vs. (polarization)^2

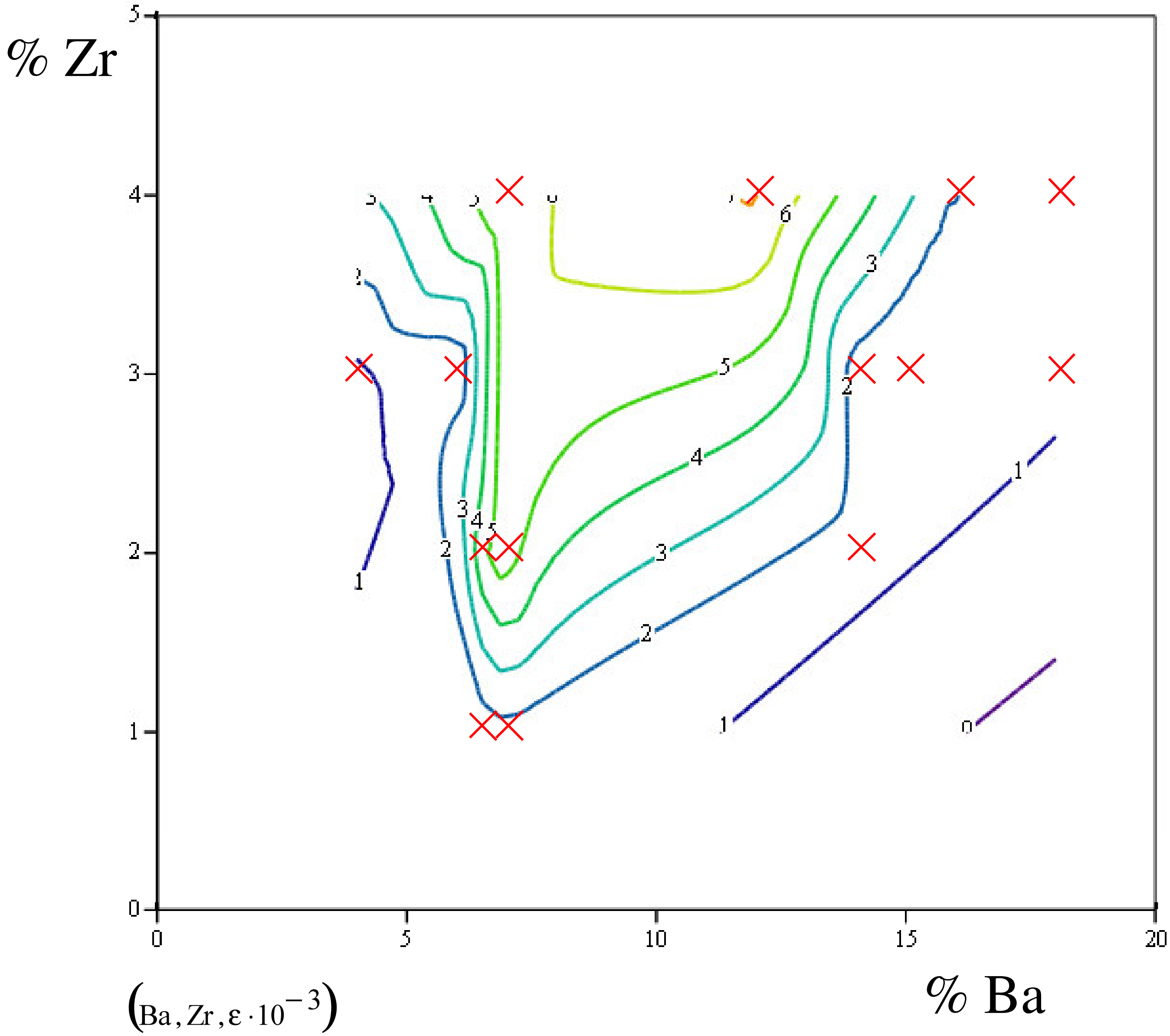
Compositional map of $Q \cdot 10^2$ (m^4/C^2)



Compositional map of large signal d_{33} (pC/N)

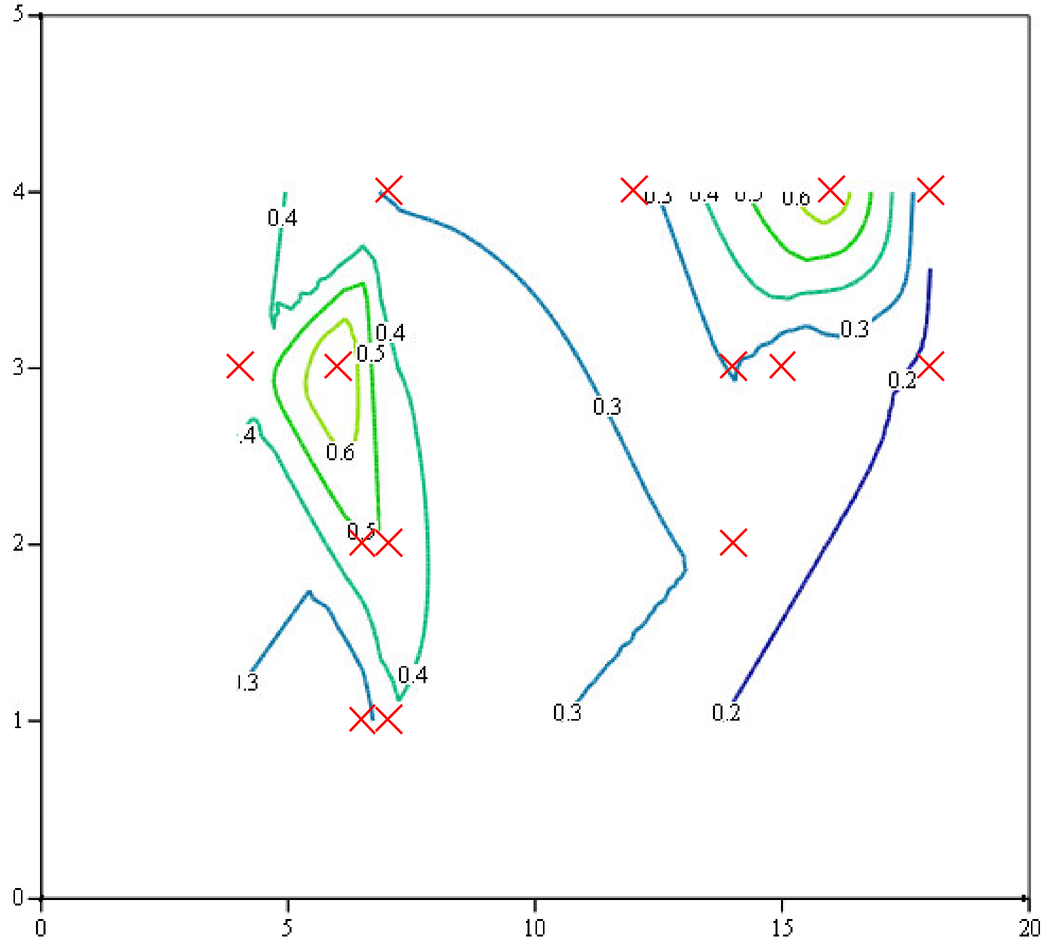


Compositional map of large signal $\varepsilon_{33} \cdot 10^{-3}$



Compositional map of relative unipolar polarization hysteresis H_P at 0.2 Hz

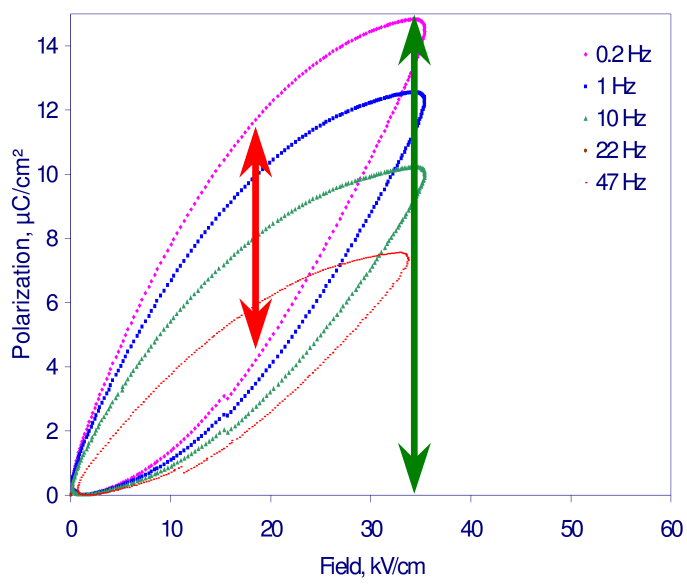
% Zr



% Ba

(Ba, Zr, dP)

$$H_P = \Delta P_{\max} / P_{\max}$$

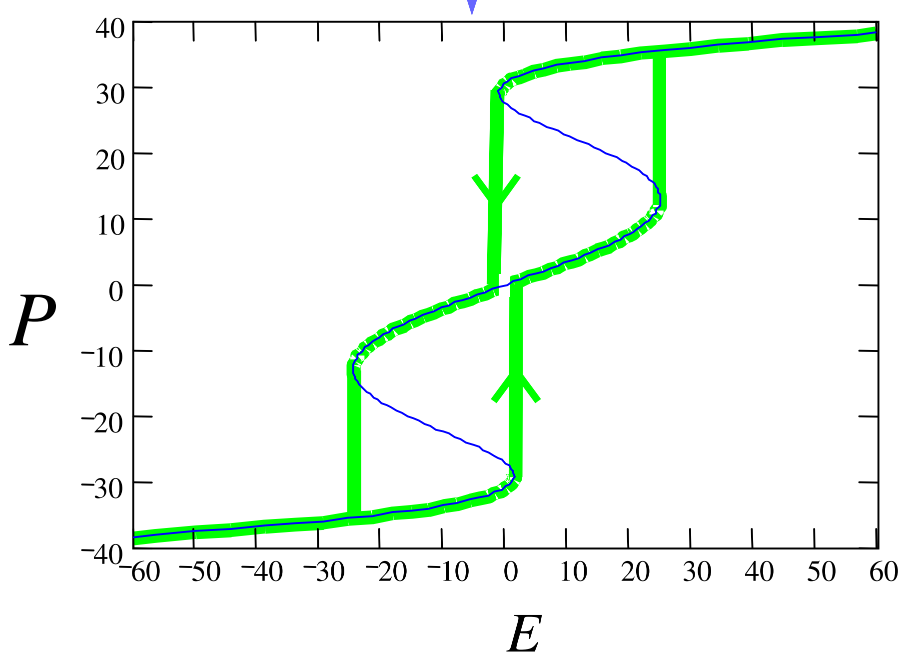


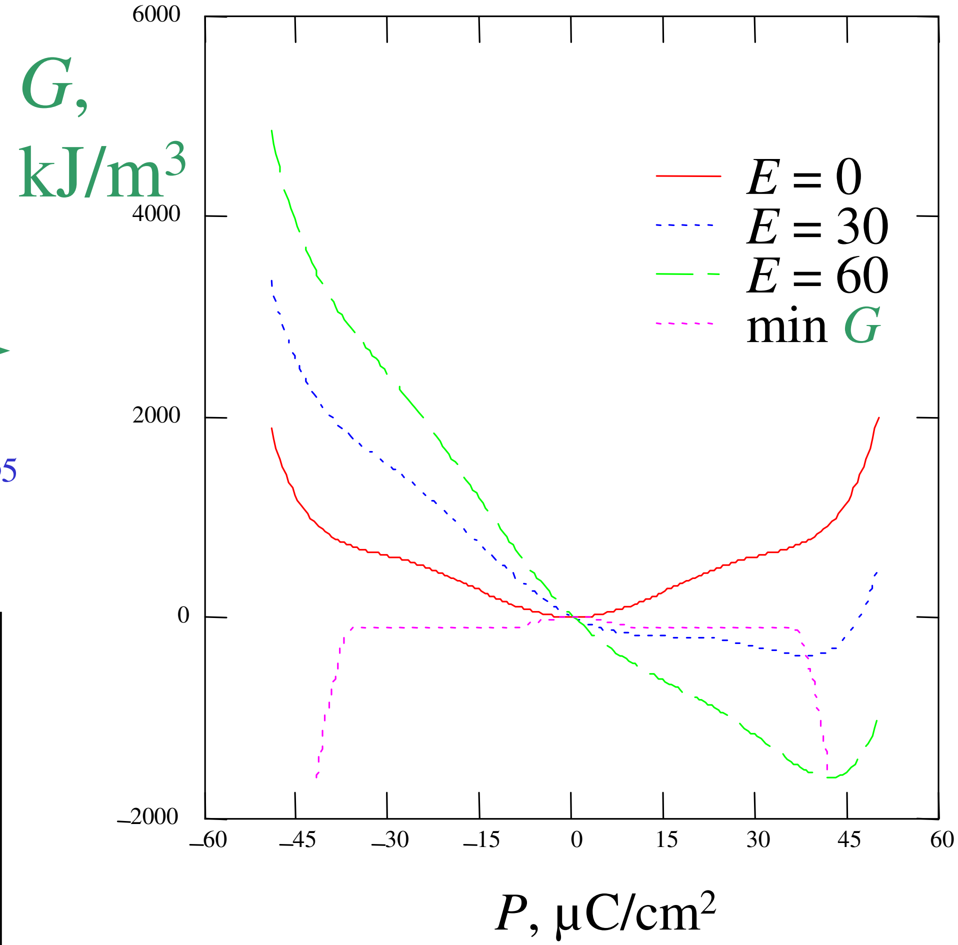
Free Energy Expansion

$$U(P) = aP^2 + bP^4 + cP^6$$

$$G(E) = U(P) - EP$$

$$\partial G / \partial P = 0 \Rightarrow E = 2aP + 4bP^3 + 6cP^5$$

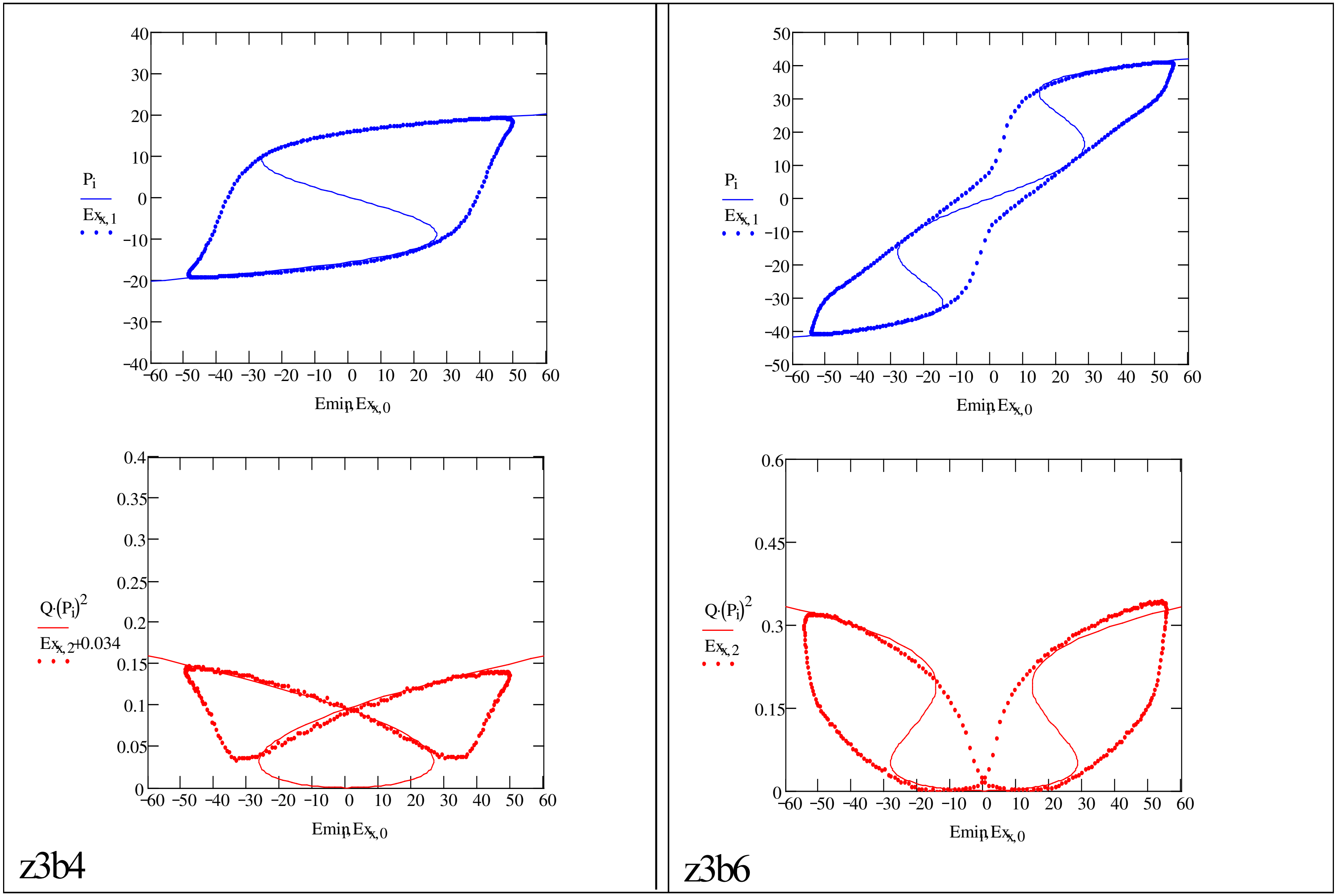


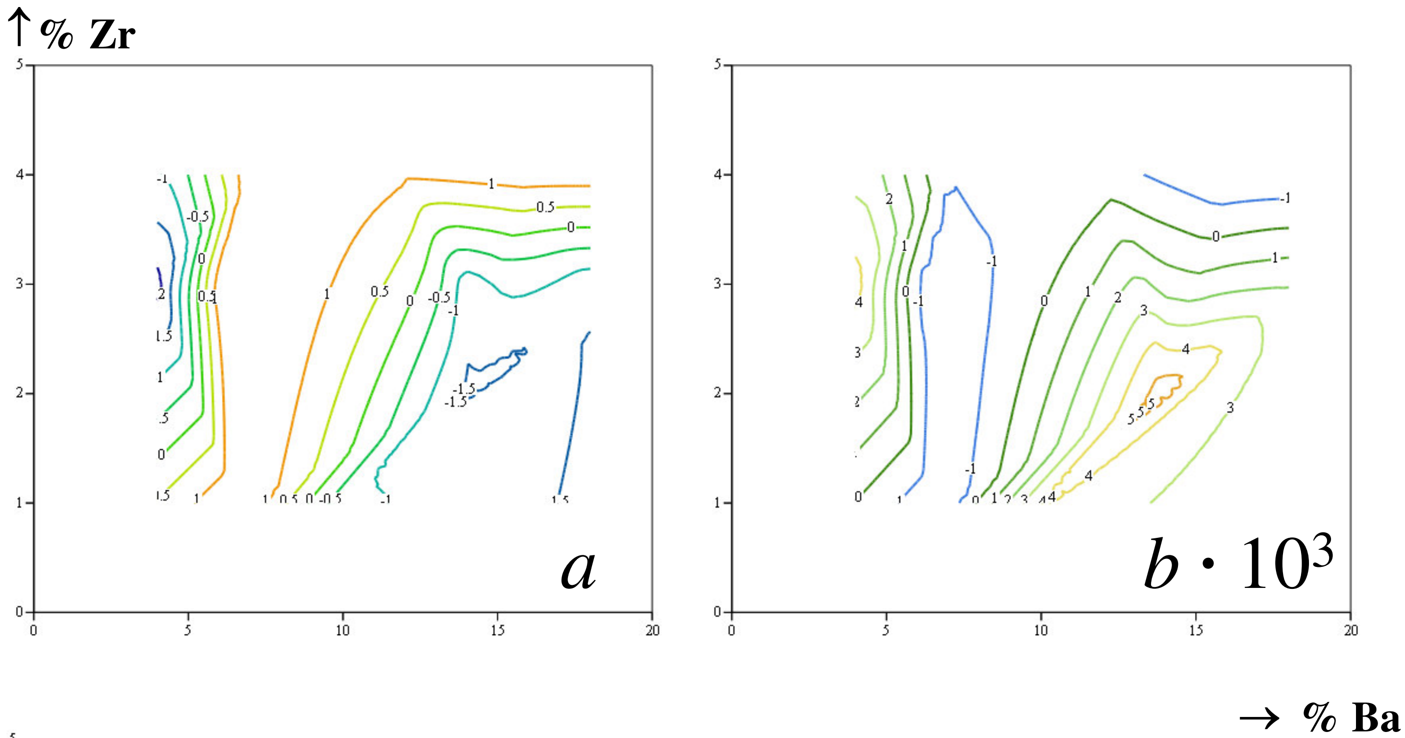


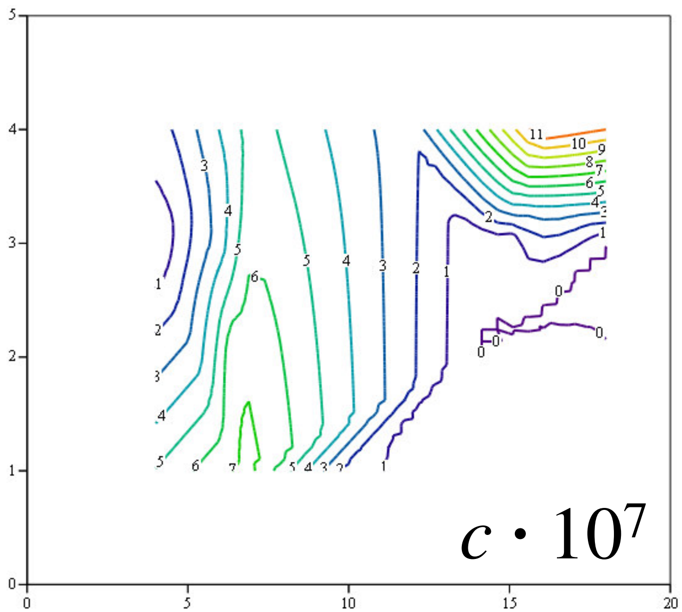
Envelope curves from free energy expansion and experimental data points

P

S

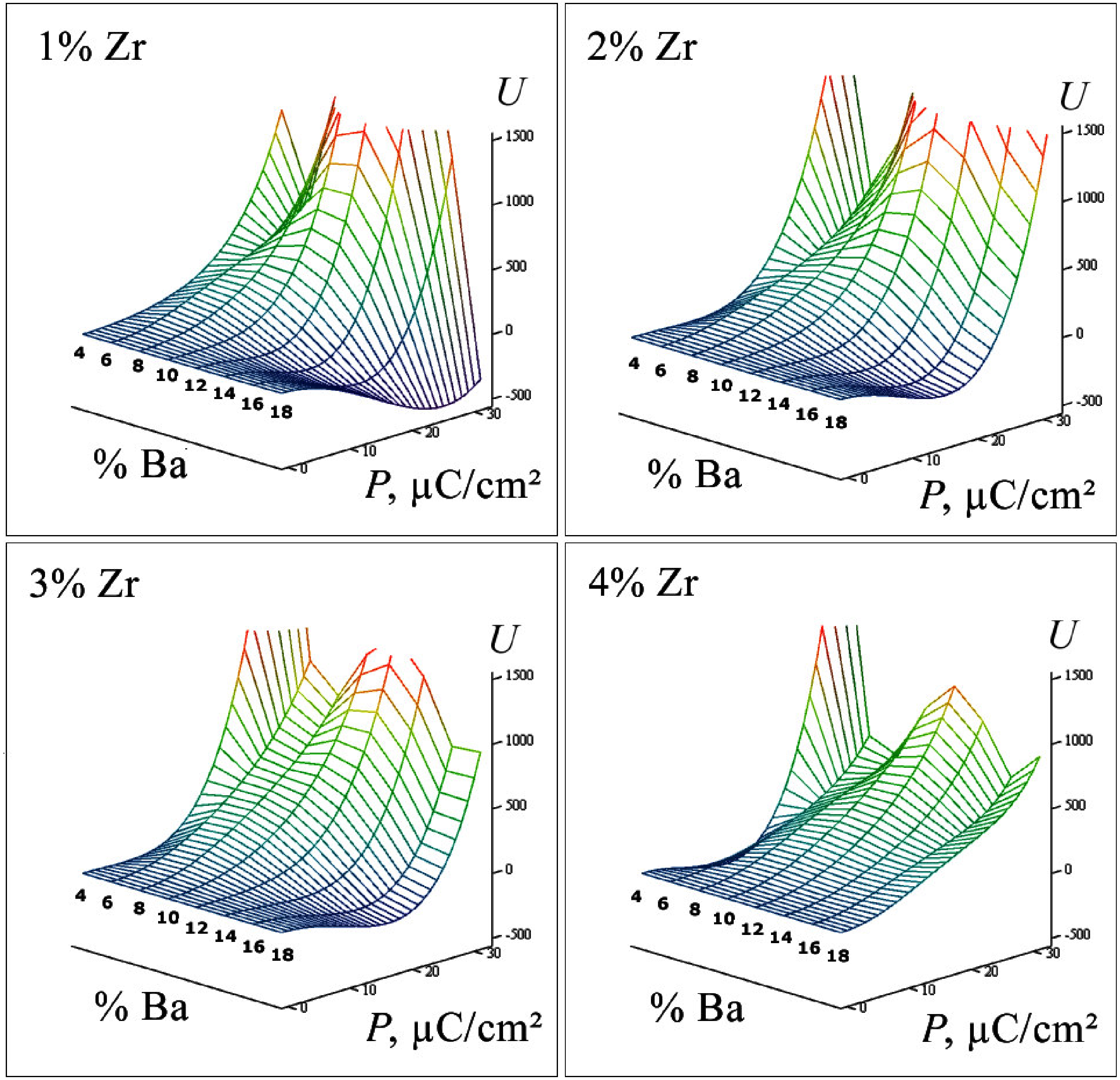


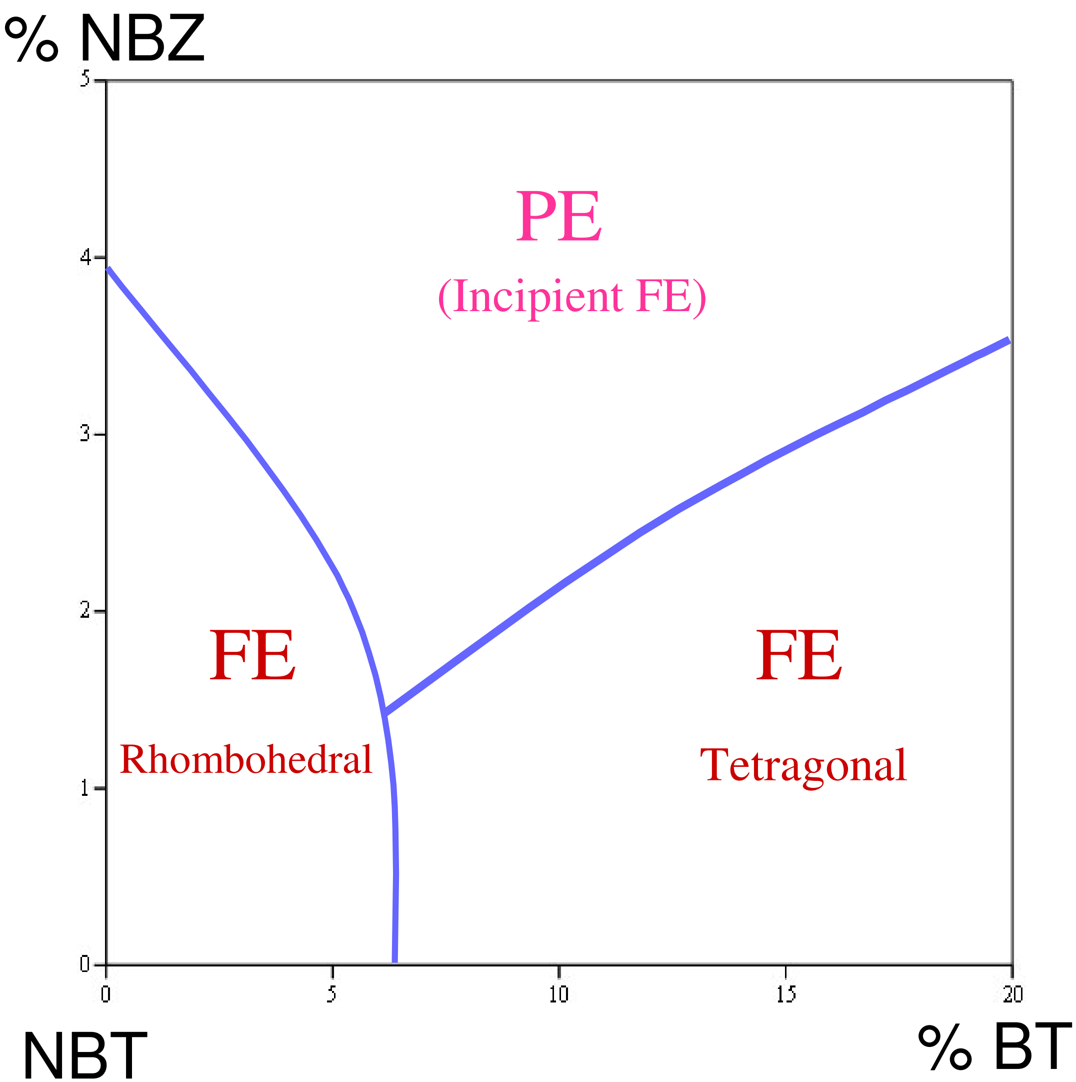




Compositional Maps of Free Energy Expansion Coefficients

Free energy U [kJ/m^3] vs. polarization P profiles



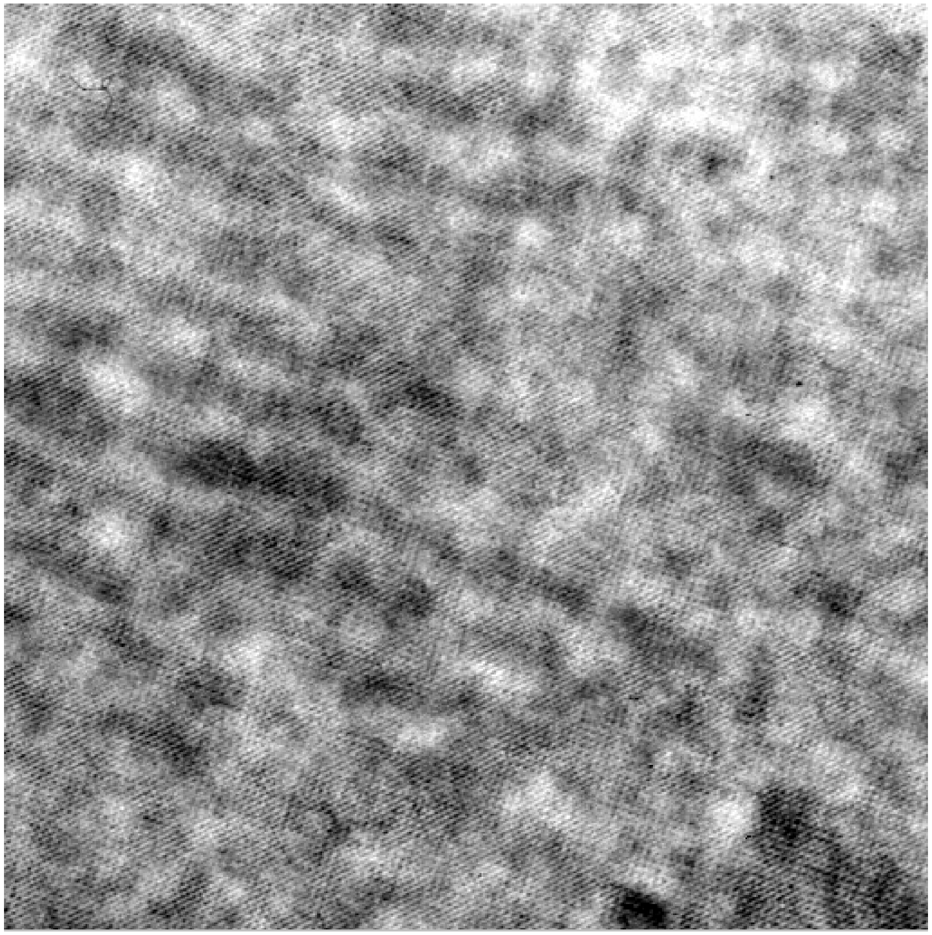


Phase Diagram Based on Electromechanical Behavior of Polycrystalline BNBZT Samples

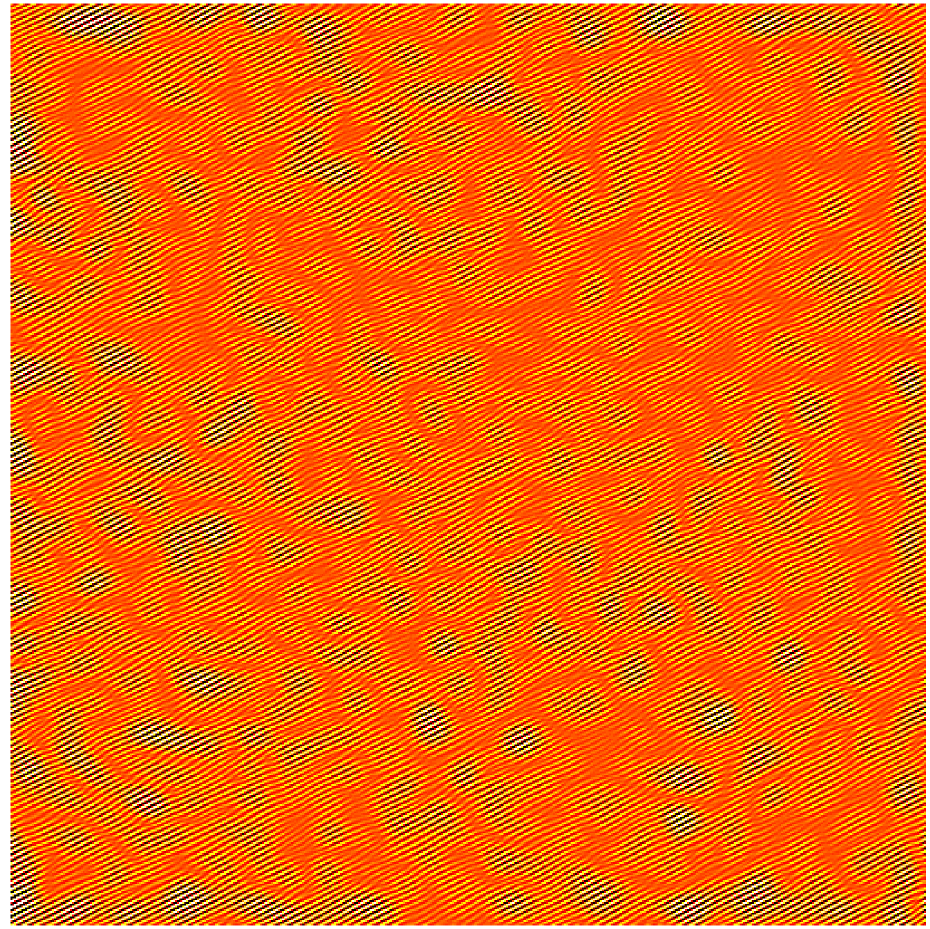
Phases:
PE—paraelectric
FE—ferroelectric

Nanostructure of High-Strain NBT-BT Crystal

[001] Raw TEM image



Fourier-filtered image

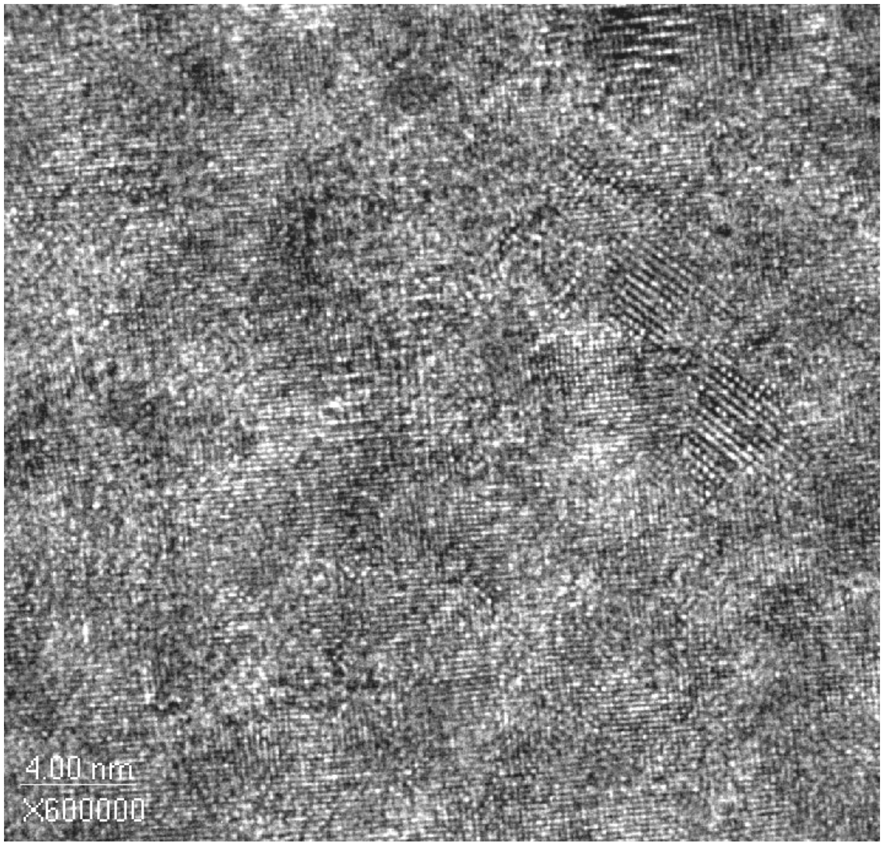


10 nm

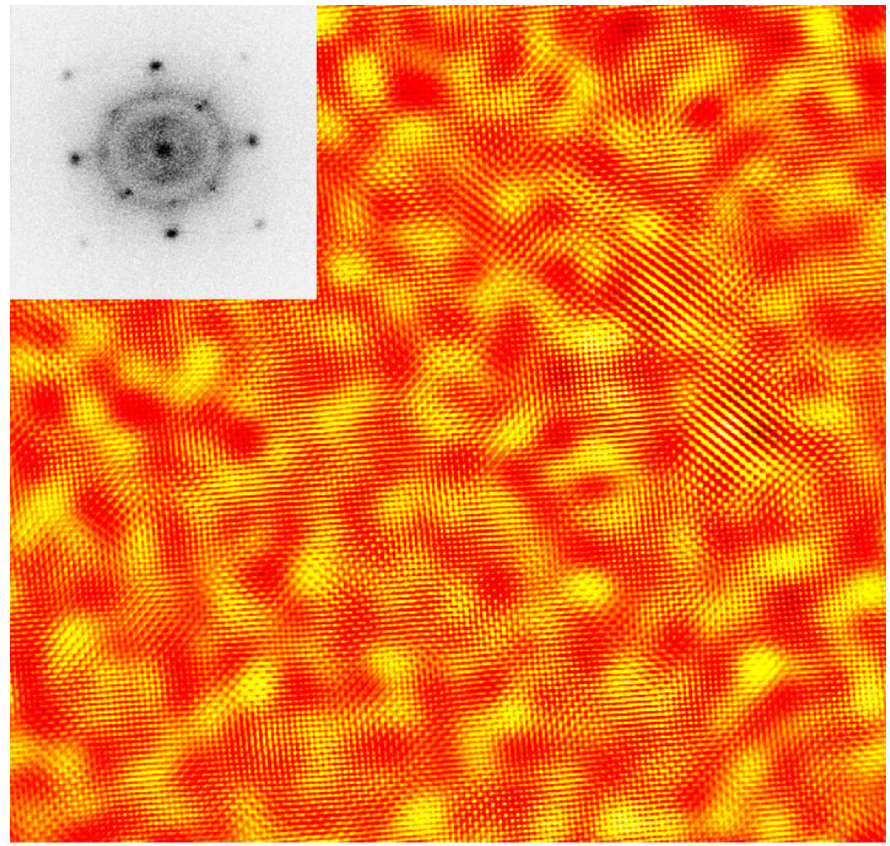
No larger scale features observed

Nanodomains in z3b6 Polycrystal

Raw [001] TEM image



Fourier-filtered image



4 nm

No larger scale features observed

Summary

- BNBZT system offers rich possibilities for lead-free ferroelectrics with high electromechanical properties
- The peak of electromechanical response has been found at the composition z2b7
- Compositional dependence of ferroelectric phase stability in the BNBZT system has been mapped by means of a free energy expansion in terms of polarization with coefficients obtained by fitting of the predicted to the observed hysteresis loops.
- Nanodomain relaxation as a mechanism of frequency dependent electromechanical response of BNBZT has been supported by microscopic observations